Ion flux through a shallow snowpack: effects of initial conditions and melt sequences

ROBERT E. DAVIS
Geophysical Sciences Branch, U.S. Army Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, New Hampshire 03755, USA

CHRISTIAN E. PETERSEN
2055 Sierra Road #53, Concord, California 94518, USA

ROGER C. BALES
Department of Hydrology and Water Resources, University of Arizona, Tucson, Arizona 85721, USA

Abstract Six snowmelt experiments were carried out under controlled conditions in a cold room to examine the effects of melt rate, melt-freeze cycles, and initial chemical distribution on the ionic pulse from a physically homogeneous snowpack. The experimental snow volume was 1 m^2 in cross-sectional area and 0.4 m deep. Different initial distributions of chemical species were prepared by introducing tracers at different stages of sieving snow into the snow container. Constant slower rates of melting caused a more pronounced removal of ions, as observed in the initial meltwaters, than did higher rates. Long melt-freeze cycles applied to a chemically homogeneous snowpack concentrated impurities at the base of the pack and produced the greatest ionic concentration in the initial meltwater collected. Short melt-freeze cycles were less effective at elevating concentrations of trace species in the initial meltwaters. As with previous experiments, the initial distribution of impurities was shown to influence the magnitude of the ionic pulse. Chemical species applied to a layer at mid-depth in the snowpack were removed slower than species applied to a layer on the top.

INTRODUCTION

Ionic pulses, which accompany the onset of snowmelt outflow from the base of snow covers, have been attributed to the heterogeneous distribution of chemical species at the microscale (ice grain) (Brimblecombe *et al.*, 1987; 1988; Bales *et al.*, 1989; Hewitt *et al.*, 1991) and the mesoscale (layers) (Bales *et al.*, 1989). Chemically heterogeneous snow covers, in which some layers have ionic concentrations much greater than others, can show more pronounced ionic pulses (e.g. Elgmork *et al.*, 1973; Davies *et al.*, 1984). Mesoscale snow chemical profiles are produced by wet and dry deposition, crystal habit, atmospheric scavenging efficiency, melt-freeze cycles, rainfall, and riming. Impurities in a snowpack are redistributed by melting, melt-freeze cycles and rainfall, which can produce increased concentrations closer to the base of the pack (Colbeck, 1981; Cadle *et al.*, 1984). The arrival of wetting fronts at the base of a snow

cover is typically sudden, removing enhanced quantities of chemical constituents (Colbeck, 1978).

At the microscale, seasonal snowpacks experience extensive recrystallization during the accumulation and ablation seasons (Colbeck, 1982). Ions such as SO_4^{2-}, NO_3^-, and Cl^- are largely excluded from the ice crystal lattice at equilibrium (Cobb & Gross, 1969; Gross *et al.*, 1987; Sigg *et al.*, 1987), and hence reside on the surface of the ice grains (Hewitt *et al.*, 1991). As metamorphism takes place, the surface area per unit volume of ice decreases, unless hoar crystals form, because the average grain size increases and fraction of the grain area occupied by bonds also increases (Davis, 1992). The hydraulic conductivity increases during this process due to the formation of larger pore spaces and less tortuous ice surfaces. Thus the mature seasonal snowpack evolves to a situation ripe for the first meltwater to remove ions at the ice-water-air interface.

Researchers have also observed preferential release of some species before others during melt. Davies *et al.* (1982) observed lower relative SO_4^{2-} and NO_3^- concentrations, compared to Cl^-, Na^+, and Mg^{2+}, in the top 3 m of a Norwegian ice cap, suggesting that the SO_4^{2-} and NO_3^- had previously been removed by percolating meltwater. Tsiouris *et al.* (1985) observed higher relative concentration peaks of SO_4^{2-} and NO_3^- than of Na^+ and Cl^- in meltwater collected after the onset of melt in the Norwegian ice cap. However, their snow cores show more of the SO_4^{2-} than Na^+ near the top of the pack, which could have contributed to higher SO_4^{2-} peaks. Similar trends were also observed by Tsiouris *et al.* (1985) in two laboratory experiments carried out at variable melt rates with homogeneous snow. In a laboratory study in which metamorphosed snow grains were aged and then washed with deionized water, Hewitt *et al.* (1991) suggested that the enrichment of SO_4^{2-} relative to Cl^- in eluting meltwater is strongly controlled by metamorphic processes.

The research reported in this paper is an experimental investigation of the movement of ionic species through a shallow, homogeneous snowpack under well-controlled conditions. The purpose of the work was to demonstrate the effects of mesoscale initial conditions and melting rates on the chemical composition of meltwater.

MATERIALS AND METHODS

We performed six snowmelt experiments in the cold laboratory at the Sierra Nevada Aquatic Research Laboratory (SNARL), University of California, near Mammoth Lakes, California.

The experimental chamber was a 1-m^2 area and 0.4-m deep box with a vinyl liner that could be removed for cleaning between experiments. Potential edge effects from the container were avoided by the large area-to-depth ratio. A thin layer of glass wool between the base of the snow and the vinyl provided liquid communication to five base drains. Prior to filling with snow, the plastic liner and the glass wool were rinsed several times with distilled water until rinse-water conductivity was less than 4 μS cm^{-1}, which was about the same as the snow used for the raw material.

Snow was collected with rinsed plastic shovels in late spring (June 1989 for experiments 1-4) and winter (January 1990 for experiments 5-6) from areas above 2700 m near Mammoth Mountain, California. Clean plastic garbage bags were used to transport snow back to SNARL and the electrical conductivity of distilled water used to rinse these bags showed no evidence of leaching from the bags.

The raw material for experiments 1-4 and 6 was damp, old snow with rounded grains that varied from 0.5 to 1.0 mm in diameter and with cluster dimensions in the range of 2-9 mm. The snow used for experiment 5 was freshly fallen new snow with much smaller grains (0.2-0.5 mm), lower density and much lower water content than the snow used for experiments 1-4. The snow was sifted through a galvanized steel sieve with 8-mm (square) wire grid. Sifting was necessary to disaggregate the sintered snow and assure small enough aggregates to achieve a relatively uniform pack.

Five of the experiments were carried out on snow with a relatively uniform distribution of chemical tracers. The exception, experiment 3, used snow with the tracers applied at two levels. This was a similar experimental setup to that reported by Bales *et al.* (1989), except that melt-freeze cycles were imposed on the snow. The experimental conditions are listed in Table 1. In each experiment tracers were applied as an aqueous mist; experiments 1, 2, 5, and 6 used both salt and acid tracers,

Table 1 Coldroom experimental conditions.

Condition	Experiment: 1	2	3	4	5	6
Date	6/89	6/89	6/89	6/89	1/90	1/90
Snowpack						
Total mass (kg)	133.3	170.0	145.5	186.9	104.9	150.7
Depth (m)	0.38	0.40	0.38	0.40	0.39	0.39
Density (kg m^{-3})	350	430	320	470	270	386
Mid-Depth Tracer						
Height applied (m)	–	–	0.20	–	–	–
Volume applied (L)	–	–	0.94	–	–	–
Solution	–	–	NaBr	–	–	–
Conc (M)	–	–	0.04	–	–	–
Top Tracer						
Height applied (m)	–	–	0.40	–	–	–
Volume applied (L)	–	–	0.94	–	–	–
Solutions/conc (M)	–	–	Na_2SO_4/0.04	–	–	–
	–	–	NaCl/0.04	–	–	–
Homogeneous tracer			–			
Volume applied (L)	4.9	4.9	–	4.9	4.9	2.5
Solution	NaCl	NaCl	–	NaCl	KCl	KCl
	NaBr	NaBr	–	NaBr	NaBr	NaBr
	Na_2SO_4	Na_2SO_4	–	Na_2SO_4	Na_2SO_4	Na_2SO_4
	NHO_3	NHO_3	–	–	HNO_3	HNO_3
Conc of each (M)	0.008	0.008	–	0.008	0.008	0.008
Melting						
Type	Continuous		Long-freeze thaw		Short-freeze thaw	
No. Cycles (h on/h off)	–	–	2(14/10)	3(10/14)	3(3/4)	6(2/2)
Melt rate[a] (mm h^{-1})	4.68	2.05	2.16	1.29	4.12	2.25
Duration of draining (h)	40.0	76.9	50.4	44.3	52.0	51
Fraction eluted	0.67	0.50	0.51	0.33	0.78	0.53
Plate temperature (°C)	43.3	23.4	25.0	25.0	35.0	33.0

[a] Depth melted, water equivalent.

experiments 3 and 4 used only salt tracers. Application of the solutions resulted in a snowpack that was 30-90 times more concentrated in Cl^-, NO_3^-, and SO_4^{2-} than the natural snow.

Snow with a relatively homogeneous distribution of species was prepared by alternately sifting 8 cm of snow into the box, applying 1/5 of the total chemical mass evenly over the 1-m^2 area and mixing the layer with trowels. This process was repeated 4 times until the snow in the box was 0.4 m deep. The layered experiment was prepared by sifting snow into the box until it was half full, applying the mid-depth tracer, then filling the box with snow and applying the top tracer. In all cases, the snow in the box was frozen by reducing the coldroom temperature to below the melting point after the experiment was set up. The snow volume was frozen to a uniform temperature between -5 and -10°C.

Snow in the experiments was melted by thermal radiation emitted from a heated black aluminum plate suspended over the top of the box. The plate temperature was maintained between 23 and 43°C for the various experiments to give melt rates comparable to rapid natural melting (Table 1). Melt-freeze cycles (experiments 3-6) conditioned the snowpack and were produced by alternately applying and removing power to the aluminum plate at fixed intervals and adjusting the temperature of the cold room to below the melting point. The number and duration of these cycles differed with each experiment (Table 1). Once energy was applied, periods between 15 and 20 h lapsed before meltwater reached the drains in the continuous-melt experiments, and 25-59 h in the melt-freeze experiments. This duration resulted more from meeting the thermal requirements of the snow volume for raising the temperature to the melting point than the actual travel time of the melt water through the snow.

Meltwater was manually collected in 4-l polypropylene beakers and with an Isco 24-bottle automatic fraction collector when the experiment was unattended. The conductivity of each sample was measured during the experiment shortly after it was collected using a Radiometer model CDM 80 conductivity meter with a CDC 314 cell; the cell constant was 3.16 cm^{-1}. An Orion model SA 520 pH meter equipped with a Ross combination pH electrode (Model 81-02) was used to measure pH during the experiment, before filtering samples. Both conductivity and pH were corrected for temperature. Samples were filtered through 0.45 m Millipore type HA filters, and split for anion and cation analysis. One drop of concentrated nitric acid was added to samples for cation analysis to prevent sorption to container walls.

Periodic profiles of bulk snow were sampled using a plexiglass coring tool with a square cross-sectional area of 100 cm^2 (Valdez, 1988). Each 2-4 cm thickness of core was transferred to a clean beaker, melted, and analyzed in the same way as the meltwater samples. The coring was carried out near the edges of the snow volume, as far as possible from the drains. Observations showed that the vertical holes left by coring did not appreciably affect the melting patterns.

Meltwater was weighed to determine total mass melted with time. Each experiment was terminated after 35 to 70% of the volume had been collected as melt, and conductivity had dropped to a consistently low level. Remaining snow was melted, weighed and discarded. We assumed that because the melt was running at low concentrations at the ends of the experiments, residual concentrations were also low. Ion chromatography was used to measure anions. The ion chromatograph consisted of a Spectraphysics model 8700 eluent pump and solvent delivery system, a Dionex AS4A

separatory column and a Dionex conductivity detector (CDM). The detection limit for Cl^-, was 0.05 mg l^{-1}, and Br^-, NO_3^-, and SO_4^{2-} all had detection limits of 0.1 mg l^{-1}. Cation analysis was performed using a Varian AA-1474 atomic absorption spectrophotometer. Detection limits for Na^+ and K^+ were 0.1 and 0.2 mg l^{-1}, respectively. Samples were analyzed in duplicate and an average value reported. The sample was analyzed a third time if the difference was greater than 10%. Usually they varied by less than 5%. The starting bulk concentration of each chemical species in the snowpack (C_a) was determined by dividing the total chemical mass of each species by the total volume of meltwater. (C/C_a) represents the concentration of a particular chemical species in a melt or core sample divided by the bulk concentration in the snowpack.

RESULTS AND DISCUSSION

Each of the experiments exhibited an ionic pulse; that is, the concentrations of ions in the initial meltwater were elevated above the bulk concentrations in the pack. Table 2 summarizes the removal of ions for the six experiments observed in the peak and final measurements.

Table 2 Removal of species in first 20% of melt.

Experiment	Percent of stated chemical species:						
	Cl^-	Br^-	NO_3-	SO_4^{2-}	Na^+	K^+	H^+
1	76	78	81	80	82	—	76
2	83	86	86	86	86	—	85
3	79	72	—	79	67	—	—
4	87	89	—	89	73	86	—
5	67	70	70	71	72	75	69
6	71	74	75	75	73	73	69

Different melt rate

The elapsed time from the start of melting to the time meltwater reached the drains varied from 15 to 59 h and the duration of each experiment varied from 60 to 110 h (Fig. 1). Melting rates were comparable to alpine snow covers, ranging from 1.3 to 4.7 mm h^{-1} (Table 1), with the greatest difference between experiments 1 and 2 for constant melting rates.

Experiments 1 and 2 had relatively uniform chemical profiles as initial conditions. The primary differences were that experiment 2 had a lower plate temperature, causing a much lower melting rate, and higher snow density (Table 1). The melt rate of experiment 2 was 40% of that in experiment 1, and initial ion concentrations were about double. (C/C_a) values of 4.5-6.5 were measured in experiment 1 and (C/C_a) values of 10-12 were observed in experiment 2 (Fig. 2(a)). Experiment 2 also had lower concentrations after 20% of the pack had melted. From 76 to 82% of each ion measured was removed in the first 20% of meltwater collected in experiment 1, while 83 to 87% of the ions eluted from the pack in the first 20% of melt in experiment 2.
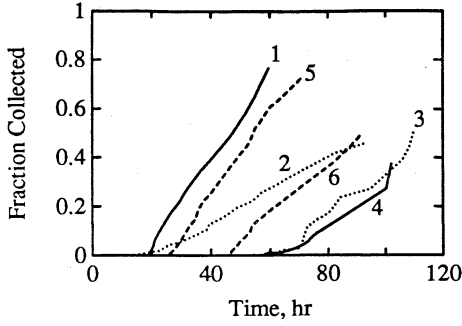
Fig. 1 Melt fractions collected versus time from beginning of first meltcycle for the six coldroom experiments. Freeze time is included for melt-freeze experiments (3-6).
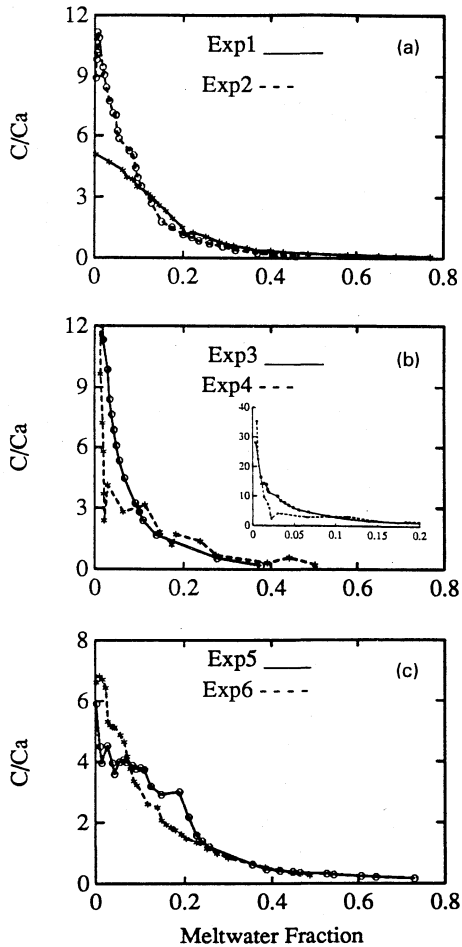
Fig. 2 Conductivity of meltwater for each of the experiments: (a) homogeneous initial condition with continuous melting (1, 2); (b) banded (3) and homogeneous (4) initial conditions with long melt-freeze cycles; (c) homogeneous initial conditions with short melt-freeze cycles (5, 6).

Greater removal of ions with lower melt rate suggests two potential effects: (1) more time for solute diffusion from concentrated immobile water at grain boundaries into the mobile meltwater front or finger, and (2) more uniformly advancing melt front, rather than the distinctly separate flow fingers we have observed at higher flow rates. Thus the lower melt rate should more efficiently leach solutes from the ice-air surface. Higher snow density generally indicates smaller pore surface area, given the same grain size, which facilitates early species removal (Colbeck, 1979). The difference in pore surface area between the snow in the two experiments was probably minor, with a small effect on the elution pattern. However, we made no stereological measurements on the snow.

At a particular location in a snow profile, ion concentrations in the snow gradually decrease as the melt wave passes due to direct leaching and diffusion of solute to mobile water from the relatively smaller volumes of concentrated immobile water. We suggest that this is a way ionic species retained in small interstices on ice grains and other zones not directly in contact with mobile water are gradually depleted. If diffusion was unimportant a much more abrupt drop in (C/C_a) values than was actually observed behind the melt wave would be expected. For example, the depth profiles in experiment 2 (Fig. 3(a)) show a gradual decrease in concentration over time after the melt wave passed. After 8 h of melting, the top of the pack had reduced ion concentrations; a concentration peak 12 cm below the surface indicated the location of the meltwave. After 24 h of melting, the highest concentrations occurred at the base of the pack, with a second peak 12 cm from the base. After 50 h of melting 20% of the pack had melted and species concentrations in the remaining pack were depleted.

Melt-freeze cycles

Experiments 3 through 6 were conditioned with melt-freeze cycles and showed peak (C/C_a) values greater than experiment 1 (Table 3). Experiments 3 and 4 were conditioned with three long melt-freeze cycles and showed the highest peak concentrations. Tracers were applied in two layers in experiment 3 and uniformly in experiment 4 (Table 1). The duration of the melt-freeze cycles was shortened for experiment 5, and duration was shortened and number of cycles increased for experiment 6, relative to experiment 4 (Table 1). Initial (C/C_a) values were 30-40 in the two experiments with long melt-freeze cycles and 5-10 in experiments conditioned with short melt-freeze cycles (Figs 2(b)-(c)). The peak (C/C_a) values were 33 to 43 in experiment 3 and similar for the anions in experiment 4, which showed lower values for the cations, ranging from 17 to 26 (Table 3). Experiments 3 and 4 showed high (C/C_a) values only in the first few samples, then a gradual decrease in (C/C_a) values similar to experiments 1 and 2 (Figs 2(a)-(b)). The conductivity curves for experiments 5 and 6 show concentration variations after the initial peak (Fig. 2(c)), probably resulting from the progress of the melt waves from successive melting cycles.

In both experiments 3 and 4 long melt-freeze cycles were associated with extremely high peak concentrations. The long melt cycles allowed the meltwaves to propagate to within a few centimeters of the base before being delayed by the freeze cycle. Moreover, concentrations in the accumulated liquid water were higher because of microscale processes during melt-freeze cycles; grain growth and grain-boundary migration were enhanced relative to the "dry-snow" case. Both processes cause segregation of impurities
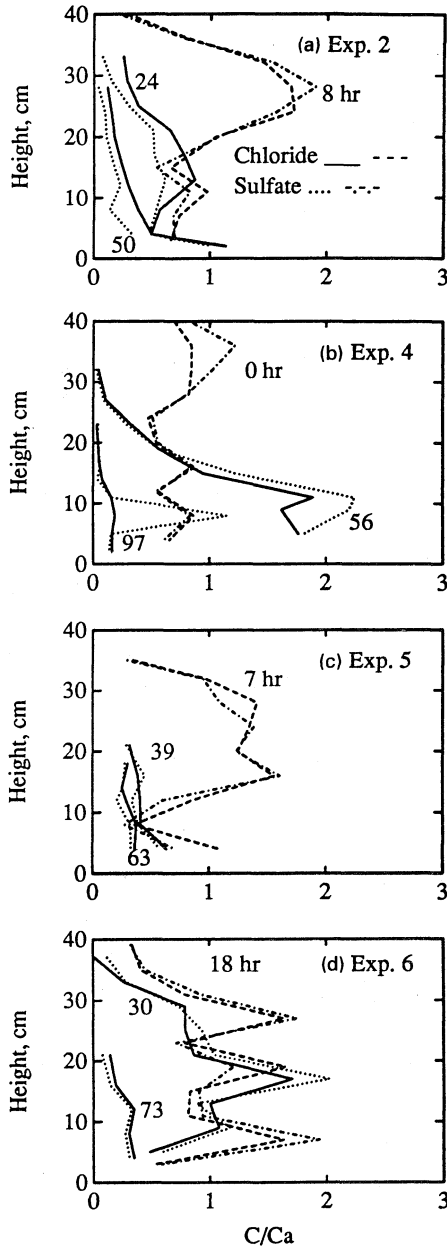
Robert E. Davis et al.

Fig. 3 Concentrations profiles of Cl⁻ and SO_4^{2-} taken during experiments; see Fig. 1 and Table 1 for sequence of melting events.

that are not readily incorporated into the crystal lattice onto a smaller area of the ice grains. With the longer cycles this process is likely over a greater vertical extent of the snow. Impurities concentrated on grain surfaces are then easily removed by liquid water flowing across the pore surface. The first depth profile in experiment 4 was taken before

Table 3 Peak and final concentration ratios.

Experiment	Cl⁻	Br⁻	NO₃⁻	SO₄²⁻	Na⁺	K⁺	H⁺	Cond.

Concentration ratio in first and (final) melt samples:

Experiment	Cl^-	Br^-	NO_3^-	SO_4^{2-}	Na^+	K^+	H^+	Cond.
1	4.6 (0.08)	4.9 (0.07)	4.8 (0.06)	4.9 (0.06)	6.3 (0.02)	– –	5.3 (0.07)	5.1 (0.08)
2	11.6 (0.12)	12.1 (0.09)	12.2 (0.08)	10.4 (0.08)	11.0 (0.07)	– –	11.5 (0.09)	11.2 (0.10)
3	42.3 (0.16)	32.9 (0.24)	– –	43.1 (0.16)	41.7 (0.38)	– –	– –	35.2 (0.10)
4	45.4 (0.18)	46.7 (0.13)	– –	43.9 (0.11)	26.3 (0.48)	17.1 (0.23)	– –	28.1 (0.18)
5	4.7 (0.19)	5.1 (0.17)	5.1 (0.16)	5.4 (0.16)	5.4 (0.19)	6.7 (0.17)	8.5 (0.19)	5.9 (0.17)
6	5.7 (0.31)	6.8 (0.26)	6.8 (0.25)	6.7 (0.25)	7.2 (0.21)	6.6 (0.22)	5.5 (0.28)	6.6 (0.27)

melting began, and showed that the initial condition was indeed relatively homogeneous. Peak concentrations were 11 cm above the base after 56 h of melting (Fig. 3(b)), with ion concentrations behind the meltwave decreasing rapidly toward the top. The 97-h depth profile showed that most ions were removed from the pack, but a slight increase with depth was still observed.

Repeated ion rejection from the lattice and removal by propagating meltwaves can cause a concentration of ions in the basal layer (Colbeck, 1981). Each melt cycle initiates a new melt wave, with those ions not removed by the initial melting more likely to be removed by subsequent waves. Of all 6 experiments, number 4 had the greatest mass of ions removed in the first 20% of the meltwater (Table 2); the initial homogeneous distribution, long melt-freeze cycles, and slow melt rate combined to produce this effect. The shorter melt-freeze cycles in experiments 5 and 6 resulted in initial concentration ratios much lower than observed for the long-duration melt-freeze cases (experiments 3 and 4). Grain scale processes segregating ions to the pore surfaces were probably constrained to the upper 10-20 cm of the snow because the short melting cycles prevented much melt water progress down into the profile. Once the final melting was started, the meltwater percolated through relatively unmetamorphosed snow in the lower portion of the experiment. Thus solutes from a smaller fraction of the snow volume were concentrated near mid depth rather than near the base of the pack. Figures 3(c) and (d) show depth profiles illustrating this.

Layered initial chemical conditions

Experiment 3 had similar initial conditions, in terms of the tracer profile, to those reported by Bales *et al.* (1989), except that it was subjected to two long melt-freeze cycles before meltwater was observed at the base. The elution sequence was similar; the

ions initially present at the top of the pack (Cl^- and SO_4^{2-}) were released sooner (Table 2) and had higher peaks (Table 3) than Br^-, which was applied only at mid-depth. Br^- eluted out with an initial (C/C_a) value of 33, compared with Cl^- and SO_4^{2-} values between 40 and 43 (Fig. 2(b)). Except for the first two samples (Fig. 2(b)), the elution curve for experiment 3 was similar to that of experiments 1 and 2 (Fig. 2(a)). By the time 20% of the meltwater was collected, 72% of the Br^- and 79% of the Cl^- and SO_4^{2-} had been removed (Table 2). Compared to the previous experiments (Bales *et al.*, 1989) the ionic pulse was enhanced substantially in experiment 3 due to melt-freeze cycles.

Differences between ionic species

In all experiments, ions with high initial peak concentration ratios were generally removed from the snow pack sooner, while those with lower initial peak concentrations were retained more by the snowpack (cf. Tables 2 *vs.* 3). In general, the differences in peak concentrations of individual ions were small. After 20% of the meltwater had been collected in experiment 1, Na^+, NO_3^-, and SO_4^{2-} had moved through the snowpack in slight preference to Cl^- and H^+. The final melt samples were high in Cl^- and H^+ but low in NO_3^- and Na^+ relative to SO_4^{2-}. In experiment 2, Cl^- was the most retained of the ions in the snowpack, SO_4^{2-} was least retained, Br^- and NO_3^- were in between. Elution concentrations and mass fractions of SO_4^{2-} and Br^- were nearly identical in experiment 4 and Cl^- and Na^+ were retained the most. Most ions eluted from the snowpack more slowly than SO_4^{2-} in experiment 5, with the possible exception of Na^+. Thus as summarized in Table 2, one finds that SO_4^{2-} and NO_3^- apparently eluted before Br^-, which eluted before Cl^-, except in experiment 3, the layered case (Fig. 4).

These weak trends agree with the elution sequence observed by Brimblecombe *et al.* (1985) and Hewitt *et al.* (1991), though they are not statistically significant. No consistent trend in Na^+, K^+, or H^+ elution relative to each other or relative to anion elution was evident, except that they always eluted before Cl^-. In these experiments, virtually all of the ions were located on the outsides of the snow grains initially and it is unlikely that any were incorporated into the crystals during the runs. On the other hand, the experiments by Hewitt *et al.* (1991) suggested that dry snow metamorphism caused preferential exclusion of solute from the ice grains. Consequently the differences in the elution of ions from the experiments were larger (Hewitt *et al.*, 1991). The
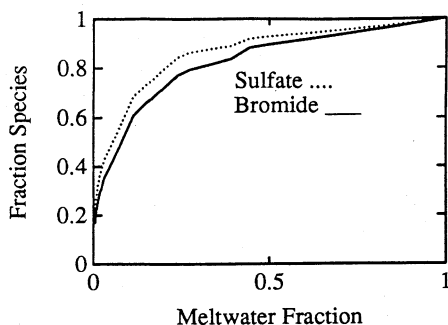

Fig. 4 Mass fraction of chemical species collected as a function of meltwater collection in experiment 3. Fractions of SO_4^{2-} and Cl^- were indistinguishable.

experiments described here suggest that there may be small effects in wet snow, leading to different elution sequences, which are caused by melt-freeze cycles and the relative mobility of different ions during snow melt.

IMPLICATIONS FOR NATURAL SNOW COVERS

Recrystallization of a snow cover prior to the melt season tends to concentrate ions on the grain surfaces. The duration and intensity of this process controls the translocation of the contaminants. Dry deposition is another mechanism by which ions are located on the outsides of snow grains. Under conditions of slow, steady melt, ions on the pore surfaces will be removed from the pack early as a concentrated peak in the meltwater (Bales *et al.*, 1989). Melting and refreezing of the snow can concentrate the pollutants at the base of the snowpack, depending on the duration of the cycles relative to the depth of the pack (cf. Bales *et al.*, 1993). Horizons in a snow cover that impede vertical water flow could also cause zones of concentrated melt to be held in the pack and released to enhance the concentration peaks of ions. This will lead to even larger concentration effects. The initial distribution of the pollutants, as demonstrated in these experiments, is also an important factor influencing the magnitude of the ionic pulse. As earlier experiments have also shown, ions higher up in the snow profile are leached earlier then those below.

CONCLUSIONS

The effects of melting rate, melt-freeze cycling and vertical distribution of impurities were examined in these laboratory experiments. Continuously melting snow at lower melt rates ($2.0 \, mm \, h^{-1}$) is more effective at removing chemical species from a snow pack than higher melt rates ($4.7 \, mm \, h^{-1}$). Lower melt rates also produced an initial meltwater pulse with higher concentrations. Melt-freeze cycles with sufficient duration to allow melt to approach the base of the snow cover resulted in meltwaters with high concentration ratios. We suggest that long duration melt-freeze cycles also cause rapid recrystallization over a greater vertical extent of the snowpack profile. These cycles cause greater segregation of impurities from the ice crystals resulting in accumulation at the grain surfaces. Long melt-freeze cycles coupled with a homogeneous initial distribution of species were most effective at removing chemical mass. Short melt-freeze cycles were less effective at significantly elevating the concentration ratios in the initial meltwater. C/C_a in initial meltwater increased with the increasing number of melt-freeze cycles.

REFERENCES

Bales, R. C., Davis, R. E. & Stanley, D. A. (1989) Ionic elution through shallow, homogeneous snow. *Wat. Resour. Res.* **25**, 1869-1877.

Bales, R. C., Davis, R. E. & Williams, M. W. (1993) Tracer release in melting snow: diurnal and seasonal patterns. *Hydrol. Processes* **7**, 389-401.

Brimblecombe, P., Clegg, S. L., Davies, T. D., Shooter, D. & Tranter, M. (1987) Observations of the preferential loss of major ions from melting snow and laboratory ice. *Wat. Res.* **21**, 1279-1286.

Brimblecombe, P., Tranter, M., Abrahams, P. W., Blackwood, I., Davies, T. D. & Vincent, C. E. (1985) Relocation and preferential elution of acidic solute through the snowpack of small, remote high-altitude Scottish catchment. *Ann. Glaciol.* **7**, 141-147.

Cadle, S. H., Dasch, J. M. & Grossnickle, N. E. (1984) Retention and release of chemical species by northern Michigan snowpack. *Wat., Air Soil Pollut.* **22**, 303-319.

Cobb, A. W. & Gross, G. W. (1969) Interfacial electrical effects observed during the freezing of dilute electrolytes in water. *J. Electrochem. Soc.* **116**, 796-804.

Colbeck, S. C. (1978) The physical aspects of water flow through snow. In: *Advances in Hydroscience* (ed. by V. T. Chow), vol. 11, 165-206. Academic Press, New York.

Colbeck, S. C. (1979) Water flow through heterogeneous snow. *Cold Reg. Sci. and Technol.* **1**, 37-45.

Colbeck, S. C. (1981) A simulation of the enrichment of atmospheric pollutants in snow cover runoff. *Wat. Resour. Res.* **17**, 1383-1388.

Colbeck, S. C. (1982) An overview of seasonal snow metamorphism. *Rev. Geophys. and Space Phys.* **20**, 45-61.

Davies, T. D., Abrahams, P. W., Tranter, M., Blackwood, T., Brimblecombe, P. & Vincent, C. E. (1984) Black acidic snow in the remote Scottish Highlands. *Nature* **312**, 58-61.

Davies, T. D., Brimblecombe, P., Tranter, M., Tsiouris, S., Vincent, C. E., Abrahams, P. W. & Blackwood, I. L. (1987) The removal of soluble ions from melting snowpacks. In: *Seasonal Snowcovers: Physics, Chemistry, Hydrology* (ed. H. G. Jones & W. J. Orville-Thomas), 337-392. Reidel, Amsterdam.

Davies, T. D., Vincent, C. E. & Brimblecombe, P. (1982) Preferential elution of strong acids from Norwegian ice cap. *Nature* **300**, 161-163.

Elgmork, K., Hagen, A. & Langeland, A. (1973) Polluted snow in southern Norway during the winter 1968-1971. *Environ. Pollut.* **4**, 41-52.

Gross, G. W., Gutjahr, A. & Caylor, K. (1987) Recent experimental work on solute redistribution at the ice/water interface. Implications for electrical properties and interface processes. *J. Physiq.* **48**, 527-533.

Hewitt, A. D., Cragin, J. H. & Colbeck, S. C. (1991) Effects of crystal metamorphosis on the elution of chemical species. *Proceedings of the Eastern Snow Conference*, 1-10.

Sigg, A., Neftel, A. & Zurcher, F. (1987) Chemical transformations in snow cover at Weissfluchjoch, Switzerland, situated at 2500 m.a.s.l. In: *Seasonal Snowcovers: Physics, Chemistry, Hydrology* (ed. by H. G. Jones & W. J. Orville-Thomas). NATO Advanced Studies Institute, Reidel, Amsterdam.

Tranter, M., Brimblecombe, P., Davies, T. D., Vincent, C. E., Abrahams, P. W. & Blackwood, I. (1986) The composition of snowfall, snowpack, and meltwater in the Scottish Highlands evidence for preferential elution. *Atmos. Environ.* **20**, 517-525.

Tranter, M., Davies, T. D., Brimblecombe, P. & Vincent, C. W. (1987) The composition of acidic meltwaters during snowmelt in the Scottish highlands. *Wat., Air Soil Pollut.* **36**, 75-90.

Tsiouris, S., Vincent, C. E., Davies, T. D. & Brimblecomb, P. (1985) The elution of ions through field and laboratory snowpacks. *Ann. Glaciol.* **7**, 196-201.

Valdez, M. P. (1988) The incorporation of sulfur dioxide into snow and depositing ice. Ph.D. Dissertation, Department of Atmospheric Sciences, University of Arizona, TuCSON.